Blending of NR/BR/EPDM by Reactive Processing for Tire Sidewall Applications. II. Characterization

Kannika Sahakaro,[1,2]* Auke G. Talma,[1,2] Rabin N. Datta,[1,2] Jacques W. M. Noordermeer[1,2]

[1]*Dutch Polymer Institute (DPI), 5600 AX Eindhoven, The Netherlands*
[2]*Faculty of Science and Technology, Department of Rubber Technology, University of Twente, 7500AE Enschede, The Netherlands*

ABSTRACT: Cure incompatibility in NR/BR/EPDM blends is a crucial problem, affecting blend properties. In a previous study, it was demonstrated that the mechanical properties of such blends can be significantly improved by utilizing a reactive processing technique, in which a pretreated EPDM is first prepared by incorporating all compounding ingredients in the EPDM and subsequent preheating, prior to crossblending with premasticated NR/BR. In the present article, the pretreated EPDM-moieties are prepared using two different accelerators, *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS) and 6-nitro MBTS. The latter was synthesized and applied for the purpose of IR characterization. The infrared (IR) spectra of the pretreated, extracted EPDM demonstrate absorption peaks associated with the IR absorption of the functional groups in the accelerator fragments, attached to the EPDM. NR/BR/EPDM (35/35/30) ternary blends are prepared by reactive mixing of the pretreated EPDM with CBS fragments attached with premasticated NR/BR on a two-roll mill. Their blend morphological features are studied using the atomic force microscopy (AFM) and transmission electron microscopy (TEM) microscopic techniques, in comparison with those of blends prepared by a conventional straight mixing method. Both the tapping mode AFM phase images and TEM micrographs clearly show that reactive mixing leads to more homogeneous blends. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2547–2554, 2007

Key words: blends; reactive processing; morphology; tire sidewall; infrared spectroscopy

INTRODUCTION

In the first part of this series[1] it has been shown that significant improvement in tensile strength and elongation at break of terpolymer NR/BR/EPDM vulcanized blends can be achieved by reactive processing of the EPDM-phase prior to mixing with the NR/BR. The reactive processing essentially consists of mixing all compounding ingredients and curatives into the EPDM-component first, then heat-treating the EPDM preblend for a duration tuned to the scorch time, subsequently mixing this pretreated EPDM into the NR/BR phase, and finally curing the resulting blend. As curatives, the most common accelerator *N*-cyclohexyl-2-benzothiazole sulfenamide (CBS) and elemental sulfur were used. The concept of grafting the mercaptobenzothiazole (MBT) moiety of the CBS onto the EPDM molecular chain was postulated. This grafting would account for an increased reactivity of the EPDM toward sulfur curing, at a speed comparable to that of NR and BR. Furthermore, the grafting of the MBT would raise the polarity of the EPDM, leading to a more homogeneous distribution of carbon black over the various phases; contrary to straight blends of the three polymers, where carbon black tends to preferentially partition toward the NR and BR phases.

In this second part of the series, the first objective is to characterize the pretreated EPDM by means of infrared (IR) spectroscopy to prove the grafting mechanism involved, as suggested in the previous study; and the second is to study the morphological features of the NR/BR/EPDM blend vulcanizates by using atomic force microscopy (AFM) and transmission electron microscopy (TEM) techniques. Both are to create a better understanding of the significant improvement in tensile properties of the blends prepared by the reactive mixing when compared with those of conventional straight mixes.

EXPERIMENTAL

Materials

The blends consist of the same ingredients as mentioned in part I. 6-Nitro-MBTS was prepared using
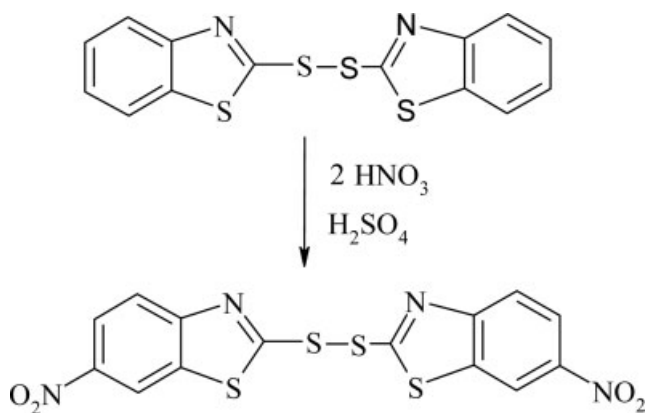
Figure 1 Preparation of 6-nitro MBTS by a direct nitration method.

2,2′-dithiobis (benzothiazole) (MBTS, 99%, Aldrich), 65% nitric acid (Merck), and 96% sulfuric acid (Fluka). Staining agent for the TEM experiment was a 2% osmic acid solution in water (Merck).

Preparation of 6-nitro-MBTS

2,2′-Dithiobis (6-nitro-benzothiazole) (6-nitro-MBTS) was prepared by a direct nitration method,[2] as shown in Figure 1, to use this as accelerator instead of the CBS in the compound formulation. Aromatic nitro-compounds have strong characteristic peaks in the IR absorption, and hence 6-nitro-MBTS was chosen for characterization purposes. 2,2′-Dithiobis (benzothiazole) (MBTS) was first slowly dissolved in concentrated sulfuric acid at room temperature, resulting in a clear dark-brown solution. The MBTS solution in acid was then cooled in ice to a temperature of 0–5°C. Subsequently, a mixture of nitric acid and sulfuric acid was slowly added. The reaction mixture was left stirring at ambient temperature for 60 min. The solid product was recovered in ice-water, filtered, neutralized by washing with water, and finally dried in a vacuum oven at 50°C. The dried product was characterized by its melting temperature, FTIR, and ^{1}H NMR spectra.

Grafting of CBS and 6-nitro-MBTS onto EPDM

The entire amounts of curatives and other ingredients, to eventually end up in the blends, were first incorporated into the EPDM only using the Brabender Plasticorder 350S mixer having a mixing chamber volume of 370 cm^3. The amounts of all compounding ingredients in the EPDM are given in Table I. The amounts in Table I (particularly the 30 phr EPDM) are to be read as the total NR/BR/EPDM (35/35/30) blend compound formulation, minus the NR and BR, as specified in Table I of part I of this series.[1] The mixer was operated with a

rotor speed of 100 rpm, fill factor of 0.7, and an initial temperature of 50°C. The EPDM was first masticated for 1 min, and then ZnO, stearic acid, and TMQ were added. After 2 min of mixing, CBS or 6-nitro-MBTS and sulfur were added and the mixing was continued for another 2 min. The final compound temperature before dumping from the mixer was in the range of 115–120°C. Immediately after dumping, the compound was sheeted on a two-roll mill to a thickness of about 2 mm. The resulting EPDM compound was tested for its cure characteristics using a Rubber Process Analyzer (RPA 2000, Alpha Technologies) at 140°C, 0.833 Hz, and 0.2° strain according to ISO 6502. Scorch time (t_{s2}), i.e., time to incipient cure was determined and used as a reference point to assign a pretreatment time of the EPDM, as detailed in the previous part.[1] A pretreatment time of scorch time minus 2 min ($t_{s2} - 2$) was used for the EPDM compound containing CBS, and a pretreatment time of scorch time minus 1 min ($t_{s2} - 1$) was applied for the one with nitro-MBTS, as indicated in Figure 2. The EPDM pretreatment was carried out in a compression molding machine (Wickert WLP1600 laboratory press) at 140°C and 100 bar using a tensile sheet mold with a thickness of 2 mm.

IR-characterization of the pretreated EPDM

1 cm × 8 cm-pretreated EPDM samples were submerged in regularly refreshed acetone for at least 48 h to extract any unreacted accelerator species. The samples were then dried in a vacuum oven at room temperature for 24 h. The IR spectra of dried samples were acquired by using the attenuated total reflectance infrared technique (ATR/IR) with a spectrometer FTS-60 (BIO-RAD Laboratories B.V., The Netherlands). The IR spectra were recorded with 512 scans at a resolution of 8 cm^{-1} in the range of 4000–600 cm^{-1}.

Preparation of blend compounds

The two types of blend compounds referred to in this work are designated according to the procedures adopted for their preparation: straight mix

TABLE I
EPDM Compounds for the Pretreatment

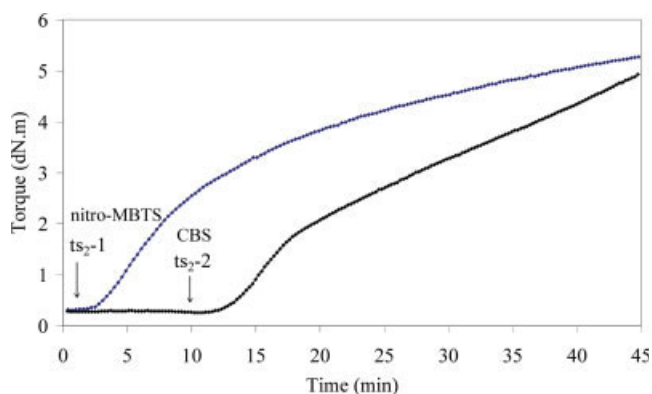| Ingredient	Weight (g)	
	CBS	6-Nitro-MBTS
EPDM	30	30
Zinc oxide	4	4
Stearic acid	2	2
TMQ	1	1
CBS	1.98 (7.5 mmol)	–
6-Nitro-MBTS	–	1.58 (3.75 mmol)
Sulphur	2.5	2.5
Total weight	41.48	41.08

Figure 2 RPA cure curves of the EPDM compounds containing CBS and 6-nitro-MBTS at 140°C with the indication of the times being used later for the pretreatment. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and reactive mix. For each of the two blend types, gum and carbon black-filled compounds were prepared. The overall recipes for both gum and filled blends are given in Table II.

The preparation of the various mixes such as gum reactive mix, filled reactive mix, gum straight mix, and filled straight mix was described in detail in part I of this series.

Vulcanization

The optimum cure time ($t_{c,90}$) of the fully compounded blends was determined as the time needed to reach 90% of the maximum torque in the RPA 2000 at 140°C, 0.833 Hz, and 0.2° strain according to ISO 6502. The blends were then vulcanized in a Wickert WLP1600 laboratory compression press at 140°C and 100 bar.

Atomic force microscopy

Vulcanized samples were prepared for AFM measurements by cryo-microtoming the surfaces of the samples with a diamond knife at –150°C using a Leica ultra microtome. The AFM images were acquired using a NanoScope III multimode atomic force microscope (Digital Instruments, Santa Barbara, CA in the Tapping Mode with phase imaging, at ambient temperature.

Transmission electron microscopy

70 nm thin sections of the blend vulcanizates were cryogenically cut with a diamond knife using a Leica ultra microtome at −150°C. The sections were deposited on a carbon support film on copper grid (200 mesh) and then vapor stained using 2% osmium tetroxide for 15 min. TEM measurements were performed with a Philips CM 30 transmission electron microscope.

RESULTS

6-Nitro-MBTS

Figure 3 shows the IR spectrum of 6-nitro-MBTS in comparison with that of MBTS. The 6-nitro-MBTS clearly shows two strong IR absorption bands at 1524 and 1346 cm^{-1} attributed to the characteristic absorption peaks of aromatic nitro- (N=O) compounds,[3,4] which normally appear at wavenumbers 1530 ± 20 cm^{-1} and 1350 ± 30 cm^{-1}.

The melting point of 6-nitro-MBTS measured by using a heating rate of 2°C/min from ambient temperature to 300°C (Stuart Scientific melting point apparatus SMP3, England) was in the range of 200–205°C, whereas that of original MBTS was in the range of 178–182°C. From the ^{1}H NMR spectra acquired using deuterated chloroform as a solvent, four different protons in MBTS were observed at 7.4, 7.5, 7.8, and 8.0 ppm, whereas three different protons in 6-nitro-MBTS resonate at 8.1, 8.4, and 8.7 ppm as a result of the nitro electron withdrawing group, as shown in Figure 4.

IR spectra of accelerator-grafted EPDM

ATR Fourier-IR spectroscopy was used in this study, since the pretreated EPDM was only partially soluble in common solvents. Even though the pretreatment step only aimed to attach accelerator fragments to the EPDM, a limited amount of crosslinking in this reactive intermediate was apparently inevitable. However, the crosslinking in the pretreated EPDM was still minimal, since the material remained processible when being mixed with NR/BR.

Figures 5 and 6 show the ATR-IR spectra of solvent extracted, pretreated EPDM prepared with CBS and 6-nitro-MBTS, in comparison with the IR spectrum of pure EPDM. The important functional groups and their assignments are listed in Table III. For pretreated EPDM with CBS, the characteristic signal of C=N is observed at 1544 cm^{-1}. For pre-

TABLE II
Formulation of NR/BR/EPDM Compounds

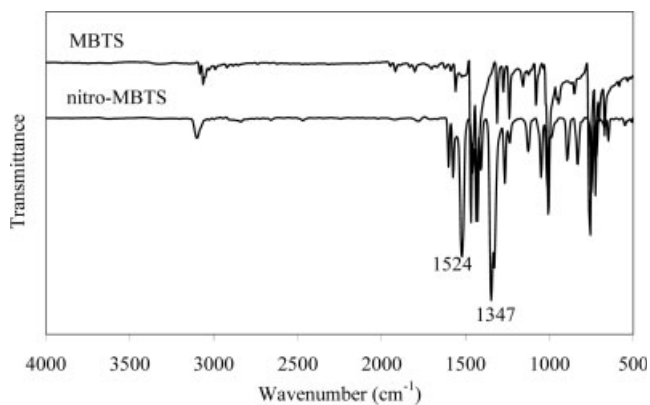| Ingredient	Gum blend content (phr)	Filled blend content (phr)
NR	35	35
BR	35	35
EPDM	30	30
Zinc oxide	4	4
Stearic acid	2	2
TMQ	1	1
CBS	1.98 (7.5 mmol)	1.98 (7.5 mmol)
Sulphur	2.5	2.5
HAF N330	–	50
Naphthenic oil	–	10
Total formulation weight	111.48	171.48

Figure 3 FTIR spectra of 6-nitro-MBTS in comparison with that of original MBTS.

treated EPDM with 6-nitro-MBTS, two strong aromatic nitro N=O absorption peaks are clearly visible at 1540 and 1401 cm^{-1}.

As these samples were solvent extracted prior to the ATR-measurement, the clear presence of earlier absorption peaks indicates a substantial amount of MBT-groups, remnants of CBS, and 6-nitro-MBT groups chemically linked to the EPDM molecular chains.

AFM images of the blend vulcanizates

The significant improvement of the tensile properties of the blends prepared using the reactive processing technique, when compared with those of blends prepared with straight mixing, is certainly also partly related to their blend morphology. In the present work, both AFM and TEM were used to characterize the morphology.

AFM works by bringing a sharp tip, located at the end of a microfabricated cantilever, into close proximity with the sample and then moving this fine tip over the sample to map the contours of the surface. The tip–sample interaction causes a change in the amplitude, the phase, and the resonance frequency of the vibrating cantilever, and hence the spatial variations of these changes can be presented in height or interaction (amplitude, phase, or frequency shift).[5–10] The height image represents surface topography, and amplitude or phase images represent micromorphological features.

In this work, the blend samples were examined using tapping mode AFM. In the tapping mode, the AFM probe is driven to oscillation at its resonance frequency by a piezoceramic element near the cantilever base, and damping of the cantilever's amplitude due
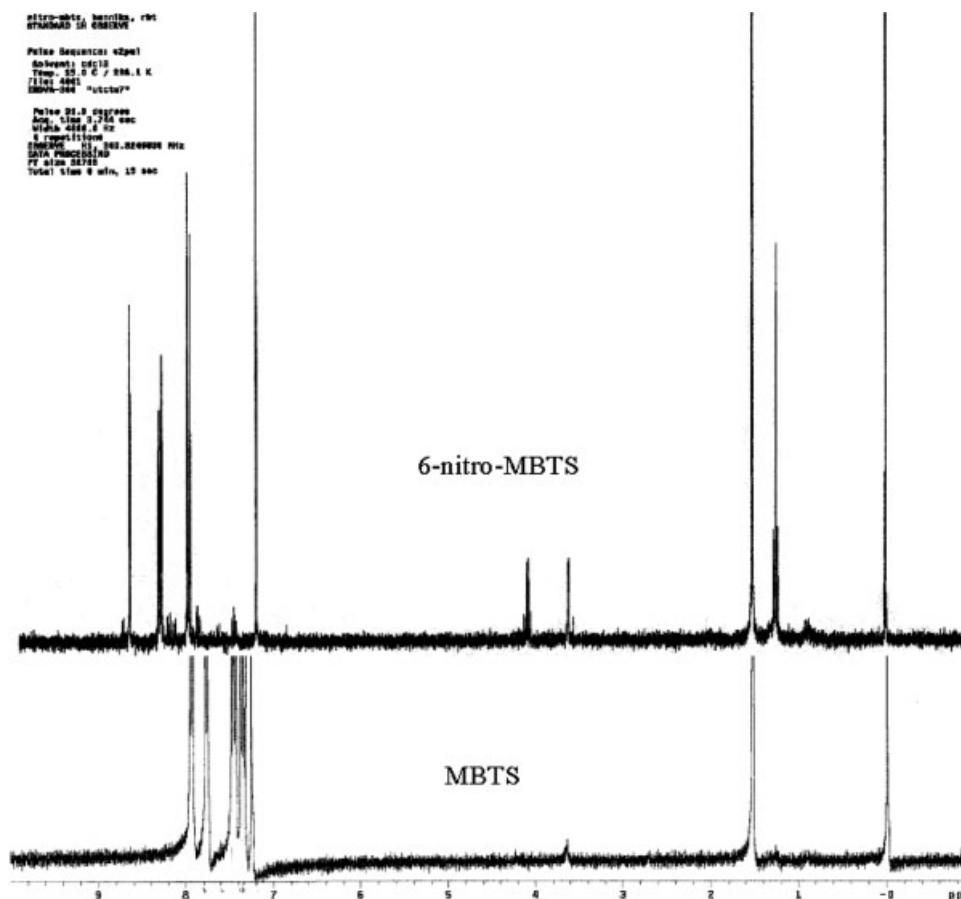

Figure 4 ^{1}H NMR spectrum of 6-nitro-MBTS in comparison with that of original MBTS.
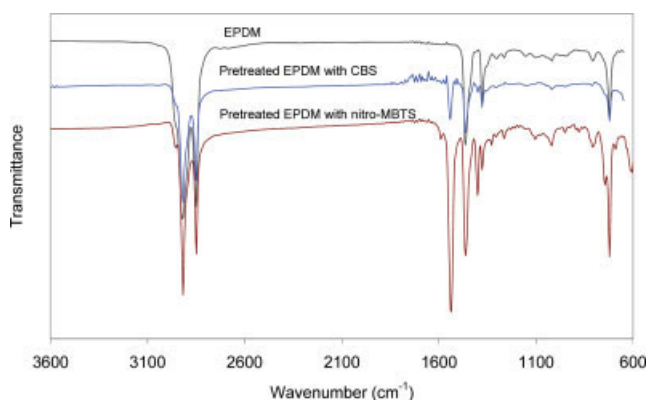
Figure 5 ATR-IR spectra of pretreated EPDM in comparison with that of pure EPDM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

to tip–sample force interaction is the mechanism used for surface profiling.[10] Figure 7 shows the phase images of gum straight and reactive mixed blends, and Figure 8 shows the phase images of the filled blends. The phase contrast is caused by differences in local elastic moduli or local hardness in the blend. Hence, differences in local crosslink density and/or local filler concentration in the ternary blends result in different tip–sample interactions and subsequently, image contrasts. In general, in the phase image obtained by tapping mode AFM, the higher modulus or harder polymer appears light and the lower modulus or softer polymer appears dark.

The phase images of the gum NR/BR/EPDM (35/35/30) blends prepared by both straight and reactive mixing in Figure 7 clearly show at least two different phases, attributed to a dark EPDM phase and a light diene (NR/BR) phase. The dark or softer EPDM phase is more distinguishable in the straight mixed blend. Considering the phase image of the blends prepared by the reactive mixing, the image shows
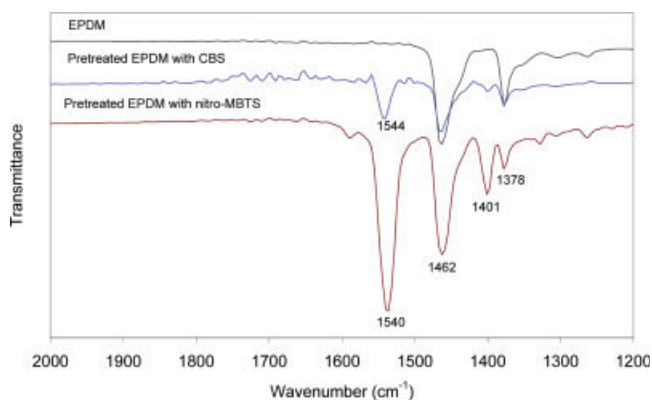
TABLE III
Infrared Absorption Peaks and Their Assignments

Infrared absorption peak (cm^{-1})	Functional group
2925, 2843	C—H stretching
1544	—C=N stretching
1540, 1401	—N=O aromatic nitro
1462, 1378	C—H bending (scissoring)
720	C—H out-of plane bending
710–570	C—S stretching, sulfides (weak)

less contrast or less distinct phases, indicating a better homogeneity of the cure state distribution. Lower cured EPDM domains do still exist, but in a lower proportion when compared with those observed in the straight mixed blend.

Figure 8 represents the tapping mode phase images of 50 phr HAF-filled NR/BR/EPDM blends obtained by conventional straight mixing (left) and by reactive mixing (right). Carbon black particles and filled polymers show a lighter phase, whereas unfilled areas appear dark. By comparing these two images, the AFM image of reactive mix on the right even more clearly illustrates a more homogeneous distribution of either carbon black or EPDM phase, or both, in the blend. The darker areas that can be attributed to the EPDM phase possessing a lower carbon black affinity when compared with the NR and BR phases are clearly smaller in the reactive mixed blend.

TEM images of the blend vulcanizates

TEM images of the gum blends are shown in Figure 9, and those of HAF-filled blends are shown in Figures 10 and 11. In the TEM,[11] the electrons pass through the sample section to a phosphorous screen. Electrons that pass through less dense areas and areas where the atomic numbers of the particles are low are scattered to a smaller extent and so hit the screen in greater number, creating more light. This is
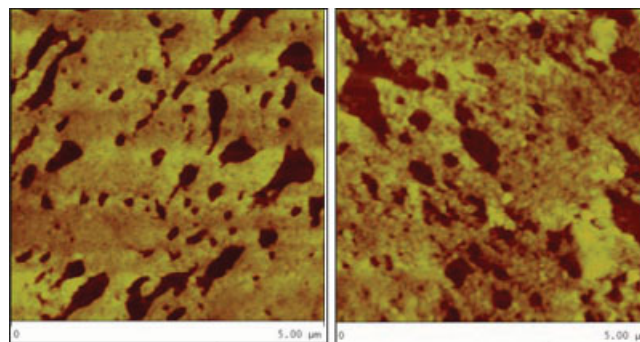

Figure 6 ATR-IR spectra of pretreated EPDM in comparison with that of pure EPDM in the range of 2000–1200 cm^{-1}. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 7 Tapping mode AFM phase images of gum NR/BR/EPDM blends: straight mix (left) and reactive mix (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
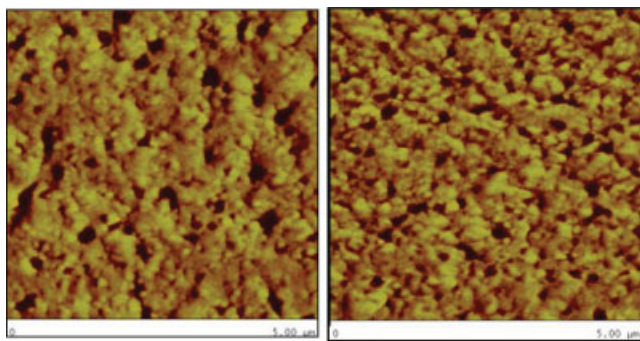
Figure 8 Tapping mode AFM phase images of 50 phr HAF-filled NR/BR/EPDM blends: straight mix (left) and reactive mix (right). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in contrast with electrons that pass through more dense areas and areas where the atomic numbers of the particles are high. Therefore, the diene phases NR and BR, which are more stained by osmium tetroxide than EPDM, become dense areas and appear dark in the images. The EPDM phase contains a very small amount of double bonds in the molecule, and is by far less stained by osmium tetroxide. The EPDM phase therefore appears light in the TEM images.

The TEM images of the gum blends in Figure 9 are complicated by the presence of the three types of rubbers in the blends. The lightest areas are the EPDM phase; however, the darker areas are a mixture of NR and BR, which cannot be clearly discerned. The EPDM particles are different in sizes and dispersed in the NR/BR phases.

Figures 10 and 11 are the TEM images of the HAF-filled blends, obtained by reactive mixing, when compared with those obtained by straight mixing. The reactive mix clearly shows a finer dispersion of carbon black among the phases. The zone
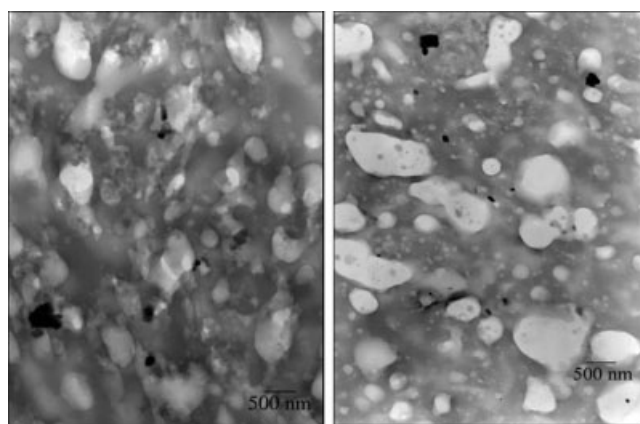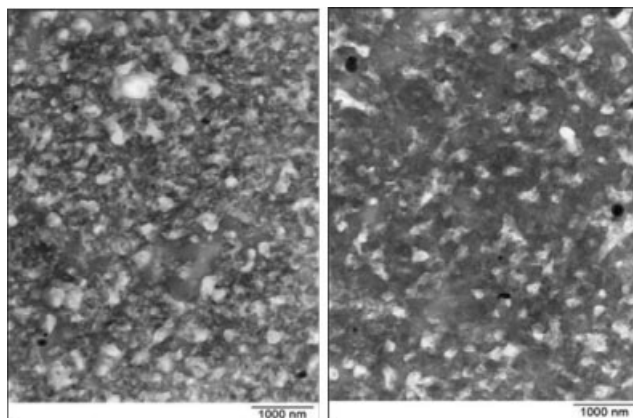

Figure 10 TEM images of 50 phr HAF-filled NR/BR/EPDM blends: straight mix (left) and reactive mix (right) at a magnification of ×10,500.

boundaries in the images of the reactive mix are less sharp, indicating a better carbon black distribution.

DISCUSSION

Pretreated EPDM

The pretreatment of EPDM by heating the compound containing sulfur, CBS or 6-nitro-MBTS, and ZnO initiates a normal sulfur vulcanization reaction. The generally accepted mechanism for sulfur vulcanization in the presence of activator ZnO starts with the generation of active accelerator complexes between accelerator and activator, which later interact with sulfur to form an active sulfurating agent. These active sulfurating agents then react with allylic hydrogen sites on the rubber molecules, resulting in a rubber bound intermediate.[12–15] Postulated EPDM-bound intermediates generated in the presence of CBS and 6-nitro-MBTS are shown in Figures 12 and 13.
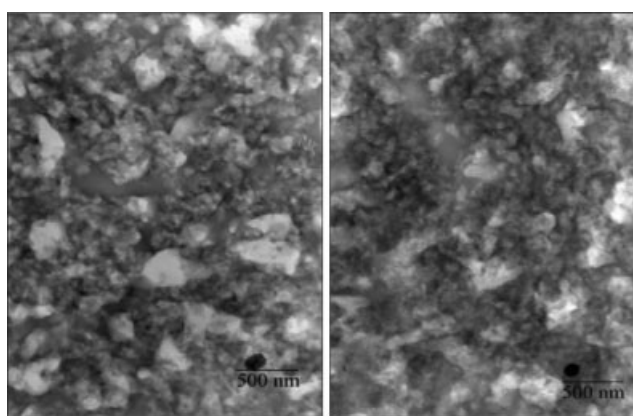

Figure 9 TEM images of gum NR/BR/EPDM blends: straight mix (left) and reactive mix (right) at a magnification of ×10,500.

Figure 11 TEM images of 50 phr HAF-filled NR/BR/EPDM blends: straight mix (left) and reactive mix (right) at a magnification of ×21,000.

Since allylic hydrogen sites are not located in the EPDM main chain, the CBS or 6-nitro-MBTS fragments must attach to the EPDM molecules at the positions provided on the third monomer ethylidene norbonene. As a result of the limited pretreatment time used, the further crosslinking reaction is quenched, and the pretreated EPDM remains processable indeed. The accelerator fragments are initially bound to the EPDM chains, and hence the migration of the curatives toward the NR/BR phase is restricted. A better curative distribution in the reactive blend consequently results in a more homogeneous crosslink distribution, which reflects in a remarkable improvement in tensile properties, as shown in our previous study.

The ATR spectra of the pretreated EPDM in Figures 5 and 6, prepared by using both the CBS and 6-nitro-MBTS accelerators, clearly show the additional peaks associated with the vibrations of the functional groups in the accelerator fragments attached to the EPDM. The CBS grafted EPDM has a distinct peak at the wavenumber of 1544 cm^{-1} attributed to the C=N stretch in thiazoles. The 6-nitro-MBTS grafted EPDM shows two distinct peaks assigned to the IR absorption of the aromatic nitro groups at 1524 and 1346 cm^{-1}. Other functional groups on the accelerator fragments, i.e., C—S and *ortho*-disubstituted benzene, are not distinguished in the spectra. The IR absorption band of the C—S stretching vibration is normally in the range of 750–570 cm^{-1}, but the assignment of this band is difficult in IR spectra, since the band is of variable intensity.[4] The *ortho*-disubstituted benzene has various absorption bands, but the intensities of most of the peaks are weak. A strong aromatic ring absorption band at 760–705 cm^{-1} is in the same range as that of the C—H out-of-plane bending in EPDM, and hence cannot be distinguished. There is a clear evidence provided by the ATR spectra to conclude that CBS-fragments and/or 6-nitro-MBTS are indeed chemically grafted to the EPDM.

Blend morphology

The AFM images of the gum blends in Figure 7 show that the dark EPDM phase is less distinct from the main phase (NR/BR) in the reactive mix, indicat-
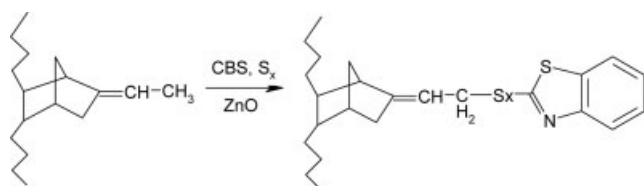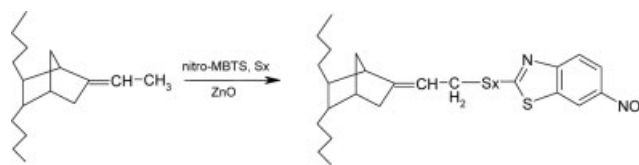

Figure 13 Postulated formation of EPDM-bound intermediate by pretreatment of EPDM compound containing 6-nitro-MBTS.

ing a better homogeneity of the cure state distribution. The pretreated EPDM does restrict curative diffusion toward the NR/BR because a large part is already chemically fixed to the EPDM, so the curative concentration is better distributed between each phase. In the straight mixed vulcanizate, the dispersed undercured EPDM phase acts as a flaw or weak point in the blend, hence resulting in inferior tensile properties. In the reactive mixed vulcanizate, lower cured EPDM domains do still exist, but smaller and in a much lower proportion when compared with those observed in the straight mixed blend.

In the AFM images of the filled blends in Figure 8, a more homogeneous distribution is most clearly observed. This can be the result of both a better crosslink distribution and/or a finer filler dispersion. The EPDM pretreatment step apparently makes it more difficult for carbon black to migrate from the EPDM phase toward the NR/BR phases. Normally, the NR/BR phases have a higher affinity for carbon black than EPDM. The grafted accelerator moieties raise the polarity of the EPDM slightly, enhancing its affinity for carbon black. Second, pretreated EPDM may already consist of a lightly crosslink network, which also hampers migration of carbon black out of the EPDM phase into the NR/BR phases.

The TEM images observed for the filled blends are in a good agreement with the AFM images. The reactive mixing leads to more homogeneous blends, and hence improves the blend properties.

CONCLUSIONS

Accelerator-grafted EPDM was prepared under a normal rubber processing condition prior to blending with premasticated NR/BR. The entire amount of curatives and compounding ingredients was first incorporated in the EPDM phase, then pretreated at elevated temperature using a predetermined time selected based on its scorch time. Extracted, pretreated EPDMs prepared using CBS and 6-nitro-MBTS as the accelerators and characterized by means of IR spectroscopy clearly show absorption peaks assigned to the functional groups of grafted accelerator fragments. Both AFM and TEM images of reactive vulcanizates of gum and filled NR/BR/

Figure 12 Postulated formation of EPDM-bound intermediate by pretreatment of EPDM compound containing CBS.

EPDM (35/35/30) ternary blends prepared by reactive mixing illustrate a better homogeneity of the blends, in comparison with those of straight mixed vulcanizates.

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